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L1 34158 S API OR ATMOSPHER? PRESSURE IONIZ? OR ELECTROSPRAY? OR IONSPRAY?
OR THERMOSPRAY? OR(ELECTRO OR ION OR THERMO OR THERMAL) (W) SPRAY?
L2 4406170 S METAL OR COPPER OR CU OR CU2 OR NICKEL OR NI OR NI2 OR ZINC OR
ZN OR ZN2 OR CHROMIUM OR CR OR CR3 OR CR4 OR ALUMINUM OR AL OR
AL3
L3 339872 S L2(4A) (DETECT? OR DETERMIN? OR MEASUR? OR MONITOR? OR ANALY? OR
ASSAY?)
L4 612 S L1 AND L3
L5 415 S L4 NOT PY>2001
L6 8 S L4 AND PATENT/DT NOT L5
L7 260 S L5-6 AND MASS SPECTRO?
L8 81 S L5-6 AND (SPECIE OR SPECIAT?)
L9 14 S L5-6 AND ISOTOP?
L10 5 S L7 AND(AUTOMAT? OR (PROCESS OR COMPUTER OR MICROPROCESSOR) (4A)
CONTROL?)
L11 11 S L7 AND DILUT?
L12 6 S L7 AND(INTERNAL STANDARD OR STANDARD ADDITION)
L13 75 S L7 AND(LIGAND OR ELEMENTAL OR IONIZATION EFFICIENCY)
L14 139 S L8-13

=> d bib,ab 1-139 l14

L14 ANSWER 1 OF 139 CA COPYRIGHT 2005 ACS on STN
AN 140:227898 CA
TI **Determination of zinc and copper isotopic ratios using ZnI-3 and CuI-3 clusters from negative-mode electrospray ionization mass spectra and internal standard approach**
AU Moraes, Maria C. B.; Brito Neto, Jose G. A.; do Lago, Claudimir L.
CS Departamento de Quimica Fundamental, Institute de Quimica, Universidade de Sao Paulo, Sao Paulo, CEP 05508-900, Brazil
SO Advances in Mass Spectrometry (2001), 15, 969-970
AB The **isotopic** ratios $63\text{Cu}/65\text{Cu}$, $64\text{Zn}/66\text{Zn}$, $64\text{Zn}/67\text{Zn}$, and $66\text{Zn}/67\text{Zn}$ were obtained from the CuI_3^- and ZnI_3^- clusters at 442.8-448.8 u. Probably there is a dependence of the **isotope** ratios on the sampling cone, multiplier, and capillary voltages. The best fit was multiplier voltage >850 V, sampling cone voltage 14 V, and capillary voltage between 1.8 and 2.0 kV.

L14 ANSWER 26 OF 139 CA COPYRIGHT 2005 ACS on STN
AN 133:315200 CA
TI **Electrospray ionization of alkali and alkaline earth metal species. Electrochemical oxidation and pH effects**
AU Ross, Andrew R. S.; Ikonomou, Michael G.; Orians, Kristin J.
CS Department of Chemistry, University of British Columbia, Vancouver, BC, V6T 1Z1, Can.
SO Journal of Mass Spectrometry (2000), 35(8), 981-989
AB The utility of **electrospray ionization mass spectrometry** (ESI-MS) for characterizing dissolved metal **species** has generated considerable interest in the use of this technique for metal **speciation**. However,

the development of accurate **speciation** methods based on ESI-MS requires a detailed understanding of the mechanisms by which dissolved metal **species** are ionized during **electrospray**. The authors report how the anal. of alkali and alk. earth metal **species** provides new information about some of the processes that affect **electrospray** ion yield. Selected metal ions and org. **ligands** were combined in 50:50 H₂O-MeCN buffered with HOAc or NH₄OAc and analyzed by flow injection ESI-MS using mild **electrospray** conditions. **Species** formed by alkali metal ions with thiol and O-donating **ligands** were detected in acidic and neutral pH solns. Electrochem. oxidn. of N,N-diethyldithiocarbamate and glutathione during **electrospray** was indicated by detection of the corresponding disulfides as protonated or alkali metal **species**. The extent of **ligand** oxidn. depended on soln. pH and the dissocn. const. of the thiol group. Tandem **mass spectrometric** expts. suggested that radical cations such as [NaL]⁺ (L = N,N-diethyldithiocarbamate) can be generated by in-source fragmentation of disulfide **species**. Greater complexation of alkali metals at neutral pH was indicated by a corresponding decrease in the relative abundance of the free metal ion. The no. of alkali metal ions bound by glutathione and phthalic acid also increased with increasing pH, in accordance with thermodyn. equil. theory. Alk. earth metal **species** were **detected** only in acidic solns., the absence of 8-hydroxyquinoline complexes being attributed to their relative instability and subsequent dissocn. during **electrospray**. Hence, accurate **speciation** by ESI-

L14 ANSWER 36 OF 139 CA COPYRIGHT 2005 ACS on STN

AN 132:354363 CA

TI **Analytical** applicability of transition **metals** and boron anionic complexes formed with iodide, chloride, cyanide, and fluoride in **electrospray mass spectrometry**

AU Moraes, Maria C. B.; Brito Neto, Jose G. A.; Do Lago, Claudimir L.
CS Departamento de Quimica Fundamental, Instituto de Quimica, Universidade de Sao Paulo, Sao Paulo, CEP 05508-900, Brazil

SO International Journal of Mass Spectrometry (2000), 198(1/2), 121-132

AB A neg.-mode **electrospray** ionization **mass spectrometry** study of some transition metal ions and B was carried out. Several expts. combining these elements with iodide, fluoride, chloride, and cyanide are presented. MeOH/H₂O was used mainly as the solvent to reduce the surface tension and, thus, the voltage at the capillary tip. Some common behaviors could be obsd. Metals give more abundant peaks with iodide and chloride, while B gives an abundant cluster for BF₄⁻. In general, the complexes are singly charged, formed by assocn. of the metal ions with the anions present in the soln., or by loss of one or more **ligands** from **species** previously present in soln. In some cases, this tendency surpasses the maintenance of the oxidn. state of the metal in liq. phase. The interconversion of low and high oxidn. states of Cu and Fe ions depends on the solvent and other **species** from the soln., but in the gas phase the high oxidn. state **species** can be reduced by collision induced dissocn. at low sampling cone voltages. Surprisingly, ferricyanide and ferrocyanide anions render almost the same spectrum. Probably [Fe(CN)₆]⁴⁻ loses one electron to a leaving solvent mol. to form [Fe(CN)₆]³⁻ in the final steps of desolvation. These and other

results suggest that, for the **ligands** studied quantitation and **speciation** are not easy tasks, but there is the possibility of performing **isotope** ratio measurements with the complexes formed with mono-**isotopic** anions. The main advantages in this case would be the shift of the m/z to high mass region, which diminishes the chance of isobaric interference, and the inexistence of hydrides, commonly obsd. in the pos. mode **electrospray mass spectrometry** spectra of metal ions and that cause isobaric interference.

L14 ANSWER 44 OF 139 CA COPYRIGHT 2005 ACS on STN
AN 132:202335 CA
TI Identification of Metal Cations, Metal Complexes, and Anions by
Electrospray Mass Spectrometry in the Negative Ion Mode
AU Mollah, Sahana; Pris, Andrew D.; Johnson, Steve K.; Gwizdala, Albin B.,
III; Houk, R. S.
CS Ames Laboratory-U.S. Department of Energy Department of Chemistry, Iowa
State University, Ames, IA, 50011, USA
SO Analytical Chemistry (2000), 72(5), 985-991
AB Pneumatically assisted **electrospray** mass spectrometry (ES-MS) was used
in the neg. ion mode for aq. metal (M) solns. in an excess of
hydrochloric or HNO₃, where the major anion X = Cl⁻ or NO₃⁻. A
collision energy of ~20 eV removes anion-solvent clusters for most
elements and leaves neg. complex ions (Mn+Xn+1)⁻. Complexation with
anions prevents charge redn. reactions at least to n = 3, even in cases
where the 3rd ionization energy of M greatly exceeds the 1st ionization
energy of the solvent. These neg. ions thus preserve the charge state
of the metal cation from the soln. and allow identification of both
cations and anions in a single set of **electrospray** conditions. Cations
such as Fe³⁺ or Cu²⁺ that have a lower oxidn. state in soln. produce a
distribution of neg. ions, each with a single neg. charge overall; e.g.,
an Fe³⁺ soln. produces both FeIIIX₄⁻ and FeIIX₃⁻. This distribution of
FeIII and FeII **species** is attributed to electrochem. redn. of Fe³⁺ at
the neg. charged ES needle. Native anions such as perrhenate or
molybdate produce singly charged analogs such as ReO₄⁻ or HMoO₄⁻.
Metal-EDTA complexes are seen as MIIIIY⁻ or MIIHY⁻. The sensitivity for
these native anions is suppressed by competition with the excess
chloride or nitrate used to produce the metal-contg. complex ions.

L14 ANSWER 49 OF 139 CA COPYRIGHT 2005 ACS on STN
AN 132:72862 CA
TI **Electrospray mass spectrometric analysis** of transition-metal halide
complexes
AU Henderson, W.; Evans, C.
CS Department of Chemistry, University of Waikato, Hamilton, N. Z.
SO Inorganica Chimica Acta (1999), 294(2), 183-192
AB A general **electrospray mass spectrometric** (ESMS) survey of uncharged
transition-metal coordination complexes contg. ancillary halide **ligands**
has been carried out, in order to det. the dominant ionization process
(es). Ionization via loss of the halide **ligand** was obsd. for most
complexes, though ions contg. coordinated solvent mols., such as MeCN,
were also seen, depending on the cone voltage employed. Protonation of
parent complexes was rarely obsd., even when **ligands** contg. basic groups
such as tri-isopropylphosphite were present, but aggregates with NH₄⁺

cations were obsd. for cis-[PtCl₂(Et₂S)₂] and for [(p-cymene)OsCl₂(PPh₃)]. In a limited no. of cases, displacement of (weakly-bonded) ancillary **ligands** as well as the halide occurred, e.g. Et₂S in cis-[PtCl₂(Et₂S)₂] and PPh₃ in [RuCl₂(PPh₃)₃] and [OsHCl(CO)(PPh₃)₃]. The formation of cleaner and more intense spectra can usually be facilitated by the addn. of a small quantity of the volatile, stronger donor **ligand** pyridine (py) to the analyte soln., resulting in [M-halide+py]⁺ ions. This forms the method of choice for the routine anal. of the majority of neutral transition-metal halide complexes, and in particular, mononuclear complexes, except when labile **ligands** are present. In the case of the dinuclear complex [Pd₂Cl₂(dppm)₂] (dppm=Ph₂PCH₂PPh₂) addn. of pyridine led to a more complex spectrum indicating a range of solvated dications formed by loss of both chlorides. A review with 51 refs.

αβσL14 ANSWER 51 OF 139 CA COPYRIGHT 2005 ACS on STN

AN 132:58386 CA

TI **Electrospray mass spectrometry: a tool for elemental speciation**

AU Stewart, I. I.

CS Institute for National Measurement Standards, National Research Council Canada, Ottawa, ON, Can.

SO Spectrochimica Acta, Part B: Atomic Spectroscopy (1999), 54B(12), 1649-1695

AB A review, with 360 refs., is given on recent progress in the development of **electrospray mass spectrometry** (ESMS) as a tool for **elemental speciation**. Reports wherein ESMS is used to qual. **det.** the presence of **metal** ions (inorg., organometallic and complexed) and nonmetallic inorg. **species** have grown exponentially over the last decade. In addn. to **elemental speciation**, impact in other areas such as gas-phase chem., inorg.-organometallic chem. and biol. **mass spectrometry** was prolific. The review is structured to cover each of the areas listed above, and also includes a brief introduction, discussion of the **electrospray** process, discussion of instrumentation and other relevant application areas. An overview of the types of **species**/complexes studied is given in each section along with a brief discussion of the application objectives and anal. aspects. Anal. considerations for the development of ESMS as a tool for **elemental speciation** are also raised, including, application, quantitation, sensitivity, limitations and future directions. The impact of **speciation** strategies involving stand-alone ESMS, ESMS coupled with online sepn. techniques and the inclusion of ESMS in dual (multiple) technique strategies are presented. High backgrounds due to chem. noise and signal suppression (matrix effects) appear to be two important factors limiting sensitive detection of most analytes. The use of sample pre-treatment, pre-concn. or sepn. techniques is necessary to alleviate these problems. Although ESMS currently suffers from a no. of limitations, continued instrumentation and methods development will improve its

L14 ANSWER 58 OF 139 CA COPYRIGHT 2005 ACS on STN

AN 131:242150 CA

TI Limitations of high performance liquid chromatography with inductively coupled plasma **mass spectrometric** detection for **speciation analysis** of trace **metals** in biological samples

AU Szpunar, Joanna; Chassaigne, Hubert; Makarov, Alexei; Lobinski, Ryszard
CS CNRS EP 132, Pau, F-64 000, Fr.
SO Chemia Analityczna (Warsaw) (1999), 44(3A), 351-362
AB Two current limitations of **speciation** anal. by HPLC-ICP MS: the difficulty to recover quant. intact metal **species** from solid samples and the difficulties with the identification of chromatog. signals were discussed. The illustrative exptl. examples include investigation of solid-liq. extn. of metal-polysaccharide complexes from a food sample with customized mixts. of enzymes. The compn. and stoichiometry of Cd, Zn - metallothionein complexes by HPLC-ICP MS and HPLC-**electrospray** (ESI) MS without and with post-column derivatization was detd. Structural characterization and quantification of cobalt complexes with macrocyclic **ligands** was studied using ESI MS and tandem ESI MS.

L14 ANSWER 66 OF 139 CA COPYRIGHT 2005 ACS on STN

AN 130:234143 CA

TI Detection of artifacts and peak identification in reversed-phase HPLC of metallothioneins by **electrospray** mass spectrometry

AU Chassaigne, Hubert; Lobinski, Ryszard

CS Laboratoire de Chimie Bio-Inorganique et Environnement, CNRS EP 132, Pau, 64000, Fr.

SO Talanta (1999), 48(1), 109-118

AB The use of **ion-spray** mass spectrometry rendered it possible to characterize the signals obtained during studies of the polymorphism of metallothionein (MT) by reversed-phase (RP) HPLC in terms of the mol. mass. Artifact signals due to incomplete metalation, exchange of metals with the impurities of the column stationary phase and cross-contamination of the preps. purified by size-exclusion and anion-exchange chromatog. may be present. On the other hand, some signals in RP HPLC with UV detection considered to belong to a single **species** were found to be composed of several complexes eluting precisely at the same time. Online **electrospray** mass spectrometry was used to systematize the knowledge of the MT isoforms and subisoforms by attributing to each of the eluting peaks the mol. mass of the form involved and can be used to compare the results obtained for the different groups.

L14 ANSWER 70 OF 139 CA COPYRIGHT 2005 ACS on STN

AN 129:285325 CA

TI **Analysis of metal species by using electrospray ionization mass spectrometry and capillary electrophoresis-electrospray ionization mass spectrometry**

AU Schramel, O.; Michalke, B.; Kettrup, A.

CS Institute for Ecological Chemistry, GSF-National Research Center for Environment and Health, Neuherberg, D-85758, Germany

SO Journal of Chromatography, A (1998), 819(1 + 2), 231-242

AB Metal **speciation** was carried out by online hyphenation of capillary electrophoresis (CE) with **mass spectrometry** (MS) via an **electrospray** ionization (ESI) interface. The com. available interface was hardly able to produce stable **electrospray** conditions over an extended period of time, mainly caused by an insufficient positioning of the CE capillary inside the ESI stainless steel tip. A device was developed, which allowed an infinitely variable adjustment of the capillary. The optimum position for stable **electrospray** conditions was set to 0.4-0.7

mm outside the ESI tip. Off-line ESI-MS studies of free metal ions [Cu (II)], metal ion-contg. complexes [CuEDTA, Me₃SbCl₂] and covalent organometallic compds. (selenocystamine, selenomethionine) were carried out to assess the suitability of the technique for metal **speciation**. The usefulness of ESI-MS as a detection method largely depends on the stability of the analyzed **species**. Inorg. **species** (i.e. metal ions) alter their compn. when being **electrosprayed**. Parts of the weakly complexing **ligands** will be exchanged by solvent mols., mainly originating from the sheath liq. The destruction of ion-solvent clusters by heating, collision-induced decompn. or use of a sheath gas may lead to charge redn. of transition metal ions. Organometallic complexes with strongly complexing **ligands** remain intact, while those with weakly complexing **ligands** suffer from the same disadvantages as inorg. **species**. ESI-MS is best suited for the **speciation** of covalent organometallic compds. The ionization process does not alter their structure and they will mostly be detected as singly charged mol. ions. The application of CE-ESI-MS for Se **speciation** to an existing method using an alk. buffer system (Na₂CO₃-NaOH) gave unsatisfactory results. The nonvolatile electrolyte affects the ESI process dramatically. The final CE method used an acidic background electrolyte (2% HOAc) for the sepn. of three organometallic Se **species** [selenomethionine (SeM), selenocystamine (SeCM) and selenocystine (SeC)]. The Se **species** were sufficiently sepd. from each other and appeared at 6.49 min (SeCM), 19.47 min (SeM) and 20.60 min (SeC). Detection limits were calcd. as 1-6 mg/l for the org. Se **species**.

αβσL14 ANSWER 72 OF 139 CA COPYRIGHT 2005 ACS on STN

AN 129:210961 CA

TI **Analysis of metal-EDTA complexes by electrospray mass spectrometry**

AU Baron, Dirk; Hering, Janet G.

CS Dep. of Geology, California State Univ., Bakersfield, CA, 93311-1099, USA

SO Journal of Environmental Quality (1998), 27(4), 844-850

AB Solns. of the strong complexing agent EDTA and Cu, Pb, Cd, Al, and Fe (III) were examd. by **electrospray mass spectrometry** (ES/MS).

Uncomplexed EDTA and metal-EDTA complexes survive the **electrospray** process intact and can be detected simultaneously by **mass spectrometry**. Best sensitivity was achieved in the pos. ion mode in which EDTA and EDTA-metal complexes (present in soln. as anions) were detected as protonated **species** with a single pos. charge. Except for the protonation, the aq. metal-EDTA complexes are preserved and neither fragmentation of complexes nor formation of clusters with more than one metal or **ligand** were obsd. in the mass spectra. Detection limits are between ~1 to 2 μM for uncomplexed EDTA and for the Cu-EDTA and Pb-EDTA complexes, with a linear range up to 10⁻⁴ M. Calibrations based on solns. with equimolar concns. of EDTA and Cu or Pb can be used to quantify EDTA-metal complexes in solns. with excess EDTA or metal, and in solns. with more than one metal present. **Isotopic** signatures of metals in the metal-**ligand** complexes are preserved, allowing the identification of the metal in a metal-**ligand** complex. **Isotopic** signatures of metals can therefore aid in the identification of metal-**ligand** complexes in unknown samples.

- L14 ANSWER 73 OF 139 CA COPYRIGHT 2005 ACS on STN
AN 129:116995 CA
TI Characterization of covalent copper and manganese organometallic complexes with Schiff bases by **ion-spray mass spectrometry**
AU Raffaelli, Andrea; Minutolo, Filippo; Feringa, Ben L.; Salvadori, Piero
CS Cent. Studio CNR Macromol. Sterordinate Otticamente Attive, Dip. Chim. Chim. Ind., Univ. Pisa, Pisa, 56126, Italy
SO Inorganica Chimica Acta (1998), 275-276(1,2), 462-469
AB Cu and Mn complexes contg. Schiff bases as **ligands**, having potential interest in homogeneous catalysis, were characterized by **mass spectrometry** using **ion-spray** ionization. Single stage **mass spectrometry** allowed the authors to confirm the mol. wt. of complexes in all cases, providing also interesting information about the real form present in soln. Complete structural characterization of the complexes was obtained by tandem **mass spectrometry**, by the anal. of the fragments formed after collisionally induced dissocn. of selected precursor ions inside the collision cell of a triple quadrupole **mass spectrometer**.
- L14 ANSWER 74 OF 139 CA COPYRIGHT 2005 ACS on STN
AN 129:89461 CA
TI The potential and challenges of **elemental speciation** by capillary electrophoresis-inductively coupled plasma **mass spectrometry** and **electrospray** or **ion spray mass spectrometry**
AU Olesik, John W.; Kinzer, Jeffery A.; Grunwald, Eric J.; Thaxton, Kurt K.; Olesik, S. V.
CS Laboratory for Plasma Spectrochemistry, Laser Spectroscopy and Mass Spectrometry, Department of Geological Sciences, Ohio State University, Columbus, OH, 43210, USA
SO Spectrochimica Acta, Part B: Atomic Spectroscopy (1998), 53B(2), 239-251
AB A review, with 47 refs., is given. Capillary electrophoresis-inductively coupled plasma **mass spectrometry** (CE-ICP-MS) and **electrospray** (ES) or **ion spray** (IS) **mass spectrometry** (MS) are recently introduced techniques for **elemental speciation**. Both techniques have the potential for rapid **elemental speciation** with low detection limits. Examples of the use of CE-ICP-MS for **elemental speciation** of pos., neutral and neg. **species** are discussed. Issues in interfacing CE and ICP-MS are considered briefly. The potential advantages and disadvantages of laminar flow in CE-ICP-MS are examd. Potential difficulties in CE-ICP-MS including loss of sample, chem. matrix effects and changes in **speciation** during sepn. are discussed. The interpretation of ES or IS-MS spectra and anal. of complex mixts. are considered. Calibration and chem. matrix effects are assessed. Potential pitfalls of interpreting bare **metal** ion spectra as **elemental anal.** are discussed. The need for fundamental understanding of the **processes** that **control** ES and IS-MS signals is examd. High cond. samples currently present difficulties for CE-ICP-MS or ES and IS-MS.
- L14 ANSWER 77 OF 139 CA COPYRIGHT 2005 ACS on STN
AN 129:12081 CA
TI **Determination of Dissolved Metal Species by Electrospray Ionization Mass Spectrometry**
AU Ross, Andrew R. S.; Ikonomou, Michael G.; Thompson, J. A. Jeffrey;

- Orians, Kristin J.
CS Department of Chemistry, University of British Columbia, Vancouver, BC,
V6T 1Z1, Can.
- SO Analytical Chemistry (1998), 70(11), 2225-2235
- AB The distribution of **metal species** in soln. was **detd.** using flow
injection **electrospray** ionization **mass spectrometry**. Complexes formed
by selected metal ions with added org. **ligands** in 50:50
water/acetonitrile and 50:50 water/methanol under acidic, neutral, and
basic conditions were detected using **electrospray** ionization conditions
optimized to best represent soln.-phase interactions. Metal **species**
contg. acetate, nitrate, and solvent mols. predominated in acidic soln.
but became less abundant at higher pH. Interactions between metal ions
and added org. **ligands** became more selective with increasing pH, showing
the expected preference of hard and soft **ligands** for metal ions of the
corresponding type. **Species** distributions also tended toward larger
complexes as pH increased. Overall ion yield was greater for aq.
acetonitrile than for aq. methanol solns.; however, redn. of copper(II)
in aq. acetonitrile resulted in the **detection** of **copper(I)** complexes for
certain **ligands**. Exptl. results for copper(II) and 8-hydroxyquinoline
in 50:50 water/methanol showed good agreement with aq. **speciation**
predicted using the thermodyn. equil. model MINEQL. Detection of neutral
complexes was achieved by protonation, deprotonation, or electrochem.
oxidn. during **electrospray**.
- L14 ANSWER 82 OF 139 CA COPYRIGHT 2005 ACS on STN
- AN 127:365440 CA
- TI **Electrospray** ionization time-of-flight **mass spectrometer** for elemental
analysis
- AU Mahoney, Patrick P.; Guzowski, John P., Jr.; Ray, Steven J.; Hieftje,
Gary M.
- CS Dep. of Chem., Indiana Univ., Bloomington, IN, 47405, USA
- SO Applied Spectroscopy (1997), 51(10), 1464-1470
- AB **Electrospray** ionization (ESI) was combined with a time-of-flight (TOF)
mass spectrometer for elemental anal. Using a heated-capillary
interface, the instrument is stable to within 5% relative std. deviation
over a 60-min period. The ratio between the **isotopes** of rubidium is
measured with a precision of 0.4% relative std. deviation for a 1-min
integration time. With the addn. of a supporting electrolyte as a spray
stabilizer and **internal std.**, the dynamic range is linear over at least
three orders of magnitude. The extent of solvent-cluster fragmentation
is governed primarily by the voltage differential between the capillary
and skimmer and, to a lesser extent, by the capillary temp. The
capillary voltage also affects the distribution of **species** among the
parent and its fragment ions for ferrocene and tetraethyllead. Under
mild interface conditions, a resolving power of 1400 is achieved for an
organolead complex. A spectrum for a larger mol., polypropylene glycol,
is presented to show the versatility of the ESI-TOF instrument for both
at. and mol. anal.
- L14 ANSWER 87 OF 139 CA COPYRIGHT 2005 ACS on STN
- AN 127:75210 CA
- TI **Electrospray mass spectrometry** as a technique for the **elemental analysis**
of **metals** and organometals

AU Zoorob, Grace; Brown, Francine Byrddy; Caruso, Joseph
 CS Department of Chemistry, University of Cincinnati, Cincinnati, OH,
 45221-0172, USA

SO Journal of Analytical Atomic Spectrometry (1997), 12(5), 517-524

AB A study of an inhouse constructed **electrospray** (ES) ion source and interface was carried out with the focus on **elemental** anal. An evaluation of the 29, 30 and 31 gauge capillary sizes for the ES source is presented. For multielement solns. of alkali metals, alk. earth metals and transition metals studied in the bare metal ion mode, the smaller 30 gauge capillary improved the detection limits by an order of magnitude over those of the larger 29 gauge. The 31 gauge was too fragile for easy handling. The ion-cluster modes of CrII, CrIII and CoII were studied and the resulting spectra indicate the possibility of attaining **speciation** information with this set-up. Matrix effects on the analyte signal of a multielement soln. of transition metals using the 29 and 30 gauge capillaries are discussed. The same trend is obsd. with both capillaries where the signal intensity improves with the addn. of 0.15% and 0.30% total dissolved solids. At higher concns. of total dissolved solids signal suppression is seen. Addnl., ES-MS was demonstrated as an **elemental** anal. tool for the study of the bare metal ion mode of larger organometallics, mainly organolead compds. and metalloporphyrins.

L14 ANSWER 88 OF 139 CA COPYRIGHT 2005 ACS on STN

AN 127:75209 CA

TI **Speciation** of chromium(VI) and chromium(III) using pneumatically assisted **electrospray** mass spectrometry

AU Gwizdala, Albin B., III; Johnson, Steve K.; Mollah, Sahana; Houk, R. S.
 CS Ames Laboratory-U.S. Department of Energy, Department of Chemistry, Iowa State University, Ames, IA, 50011, USA

SO Journal of Analytical Atomic Spectrometry (1997), 12(5), 503-506

AB Mass spectra can be obtained from aq. solns. contg. both Cr³⁺ and Cr₂O₇²⁻ as neg. ions under the same spray conditions. An excess of HCl is used so that Cr³⁺ sprays as an anionic chloro complex. Moderately energetic collision conditions produce CrO₃⁻ from CrVI and CrOCl₂⁻ from CrIII. Detection limits are 100 and 60 ppb for CrIII and CrVI, resp. Reasonable calibration curves are provided by plotting the ratio of the analyte signal to that for ³⁷Cl⁻.

L14 ANSWER 89 OF 139 CA COPYRIGHT 2005 ACS on STN

AN 127:70420 CA

TI **Ion spray mass spectrometry** for **elemental speciation** in aqueous samples: preliminary investigation of experimental parameters, matrix effects and metal-ligand complexation

AU Olesik, John W.; Thaxton, Kurt K.; Olesik, Susan V.
 CS Laboratory for Plasma Spectrochemistry, Laser Spectroscopy and Mass Spectrometry, Department of Geological Sciences, The Ohio State University, Columbus, OH, 43210, USA

SO Journal of Analytical Atomic Spectrometry (1997), 12(5), 507-515

AB **Ion spray** mass spectra obtained from aq. solns. are discussed. Ion clusters with large nos. of water mols., very few water mols., or bare **elemental** ions were obtained by adjusting the sampling orifice voltage, skimmer voltage, or position of the **ion spray** nebulizer relative to the

sampling orifice. In some cases, sub-mm changes in the **ion spray** nebulizer position can dramatically affect the nature of the obsd. spectra. There was evidence of declustering between the skimmer and first ion lens and between the sampling orifice and skimmer. Mass spectra interpretation must be conducted with care since potential spectral overlaps are common. Using a triple quadrupole **mass spectrometer** allows assessment of potential spectral overlaps. Ni-EDTA complexation was studied. The Ni⁺ signal correlated with the expected concn. of free metal ions in the soln. not the total metal concn., even when relatively harsh conditions that produced bare metal ion spectra were used. Matrix effects due to high NaCl and HCl solns. were briefly studied.

L14 ANSWER 95 OF 139 CA COPYRIGHT 2005 ACS on STN

AN 126:165843 CA

TI Investigations into chromium **speciation** by **electrospray** mass spectrometry

AU Stewart, Ian I.; Horlick, Gary

CS Dep. of Chem., Univ. of Alberta, Edmonton, AB, T6G 2G2, Can.

SO Journal of Analytical Atomic Spectrometry (1996), 11(12), 1203-1214

AB Chromium is an element whose toxicity is oxidn. state dependent. Chromium(VI) is considered toxic to humans whereas Cr(III) is considered to be an essential nutrient. It therefore becomes important to be able to distinguish between the two oxidn. states in soln. **Electrospray** mass spectrometry (ESMS) has the potential to provide useful information on chromium **species** in soln. samples. The various soln. forms of both oxidn. states may be obsd. directly and are presented. Other more uncommon **species** of both oxidn. states such as polymeric Cr(III) and the polyanion trichromate are discussed. Finally, the ability of ESMS to monitor other aspects of the soln. chem. of both chromium oxidn. states is explored.

L14 ANSWER 101 OF 139 CA COPYRIGHT 2005 ACS on STN

AN 125:315481 CA

TI Comparison of **electrospray** and inductively coupled plasma sources for **elemental** analysis with **mass spectrometric** detection

AU Brown, Francine Byrde; Olson, Lisa K.; Caruso, Joseph A.

CS Dep. Chem., Univ. Cincinnati, Cincinnati, OH, 45221-0172, USA

SO Journal of Analytical Atomic Spectrometry (1996), 11(9), 633-641

AB Both the qual. and quant. aspects of **electrospray** (ES) and ICP sources were investigated using the same **mass spectrometer** (originally a VG PlasmaQuad I instrument). While it is well established that ICP-MS is a powerful tool for **elemental** anal., **electrospray** ES-MS has recently become popular as a promising **elemental** anal. technique that can complement the detection capabilities of ICP-MS. The inhouse constructed ES source efficiently produced the bare singly charged metal ion and the optimum ES source conditions varied depending on the charge redn. required to attain the singly charged state. The day-to-day signal reproducibility was excellent (5% RSD), and the removal of the photon stop increased ion transport to the detector. A comparison of the figures of merit for Rb, Cs, Ba, V, Cr, Ni, Co, Cu, Zn and U showed that the detection limits obtained by ES-MS (ng ml⁻¹) are only 2-3 orders of magnitude higher than those found using the ICP source.

Addnl., Ca was detd. in NIST SRM 1643c (Trace Elements in Water) by ES-MS.

L14 ANSWER 111 OF 139 CA COPYRIGHT 2005 ACS on STN

AN 124:163611 CA

TI **Isotope Ratio Measurements with Elemental-Mode Electrospray Mass Spectrometry**

AU Ketterer, Michael E.; Guzowski, John P., Jr.

CS Department of Chemistry, John Carroll University, University Heights, OH, 44118, USA

SO Analytical Chemistry (1996), 68(5), 883-7

AB The **isotope** ratio capabilities of an **electrospray** ionization source interfaced to a quadrupole **mass spectrometer** are described. With the instrument operated in the **metal** ion mode, **isotope measurements** of Ag, Tl, and Pb are conducted using **elemental** ions produced from 1×10^{-4} M solns. of metal nitrates or acetates in MeOH. For Ag and Tl, spray conditions are identified that produce spectra free of MH⁺ ions. Unbiased Ag and Tl ratio measurements with precisions of ~0.2% relative std. deviation are readily attained. Further improvement in relative precision appears to be limited by temporal drift in the degree of mass discrimination imparted to the measurements by the **mass spectrometer**. **Isotopic** anal. of Pb is greatly complicated by significant yields of PbH⁺ polyat. ions.

L14 ANSWER 118 OF 139 CA COPYRIGHT 2005 ACS on STN

AN 123:24729 CA

TI A Role for **Electrospray Mass Spectrometry** in Electrochemical Studies

AU Bond, Alan M.; Colton, Ray; D'Agostino, Antonella; Downard, Alison J.; Traeger, John C.

CS Department of Chemistry, La Trobe University, Bundoora, 3083, Australia

SO Analytical Chemistry (1995), 67(10), 1691-5

AB The advantages of coupling bulk electrolysis with **electrospray mass spectrometry** (ESMS) are demonstrated using the oxidative electrolyses of copper, nickel, and cobalt diethyldithiocarbamates (Cu(Et₂dtc)₂, Ni(Et₂dtc)₂, and Co(Et₂dtc)₃). Both online and off-line methods were developed to detect the charged **species** formed in the oxidn. processes ([Cu(Et₂dtc)₂]⁺, [Ni(Et₂dtc)₃]⁺, and [Co₂(Et₂dtc)₅]⁺, resp.) using common electrochem. solvents and electrolyte (acetonitrile, dichloromethane, and tetrabutylammonium hexafluorophosphate (Bu₄NPF₆)). In the off-line mode, conditions are established for electrolyses of solns. contg. equimolar (2 mM) electroactive compd. and electrolyte. Following **diln.**, an excellent signal-to-noise ratio is obtained for the ES mass spectrum of the electrolysis product. Online electrolysis with ESMS detection of charged soln.-sol. products (a new form of spectroelectrochem.) is achieved using a simple flow cell constructed from two lengths of Pt microtubing. The outlet of the cell is connected directly to the fused silica capillary of the spectrometer, and after electrolysis of an acetonitrile soln. contg. 0.2 mM electroactive compd. and 0.2 mM Bu₄NPF₆, the product is detected with high sensitivity. The methods should be readily applied to most other common electrochem. solvents and electrolytes.

L14 ANSWER 120 OF 139 CA COPYRIGHT 2005 ACS on STN

AN 122:229213 CA
TI **Ionization efficiency** of dicopper complex in **electrospray ionization mass spectrometry**
AU Lee, Mei-Kuei; Ling, Yong-Chien; Huang, Pie J.; Wang, Sung M.
CS Department of Chemistry, National Tsing Hua University, Hsinchu, 30043, Taiwan
SO Journal of the Chinese Chemical Society (Taipei) (1994), 41(6), 711-17
AB Dicopper complex **Cu₂(PDTB)(ClO₄)₄** was **analyzed** by **electrospray** technique under varied conditions to study the effects of important factors on **ionization efficiency**. The factors taken into account are spray voltage (Vn), temp. of the drying gas, needle layer distance (Dnl), potential difference between the capillary and skimmer (Vcs), p.d. between skimmers 1 and 2 (Vss), and concn. of analyte. The total ion current increases proportionally with Vn varied from 2.0 to 4.0 kV. The ionic states are not influenced by the variation of Vn and temp. of the drying gas. Variation in nebulization efficiency caused by varied Dnl appears to influence the detected ions in several ways. Structurally characteristic ions are preserved with Vcs smaller than 50 V, dissociate into fragments of smaller molar mass with Vcs 80 V or greater, and disappear with Vcs 200 V or greater. Vss influences the relative intensities of detected ions by an effect of ion focusing. The dependence of the intensity of detected ions on analyte concn. at 10⁻⁴ M or greater is ascribed to the principle of equil. in soln.

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